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Fluorescence behaviour of cyanobiphenyl liquid crystal molecules in liquid crystal/polymer composite films

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The fluorescence behaviour of the liquid crystal, 4-cyano-4′-pentylbiphenyl (5CB), in composite thin films prepared by the photopolymerization of 5CB/diacrylate mixtures, was investigated by means of three different excitation methods, in which the total-internal-reflection or surface-limited excitation method was used for analysis of the fluorescence from an ultra-thin interface layer (<100 nm) in contact with the substrate surface, whereas the fluorescence from the interior bulk was analysed by the through-film excitation method. It was found that intensity ratios of the monomer and excimer emissions of 5CB are significantly lower in the interface layer than in the interior bulk, depending upon photopolymerization conditions as well as upon the structures of the diacrylates used. Scanning electron microscopic observations and light-scattering measurements of some typical composite films showed possible relationships between morphological features and fluorescence characteristics depending upon the diacrylate structures and polymerization conditions. The different fluorescence behaviour has been discussed in terms of differences in mobility and/or aggregation degrees of 5CB molecules arising from dominant molecular interactions with the substrate and polymer surfaces.

1. Introduction

Composite thin films of liquid crystals (LCs) and polymers are materials of considerable current interest associated with light control and electro-optic applications, since such films sandwiched between two transparent electrodes can be switched from a light-scattering ‘off’ state to a transparent ‘on’ state upon applying a modest electric field to the electrodes [1]. A convenient way for the preparation of such LC/polymer composite thin films is the phase separation induced by *in situ* photopolymerization of homogeneous mixtures of a LC and a prepolymer sandwiched between two electrodes, giving inhomogeneous materials with different features depending upon LC/prepolymer feeding ratios and other polymerization conditions [2]. For instance, a polymer-stabilized LC material consisting of a continuous LC phase in a polymer network may be formed at high LC/prepolymer ratios, whereas at lower feeding ratios the photopolymerization may yield a polymer-dispersed LC material in which the LC droplets are dispersed in a polymer matrix. Moreover, the morphology of such composite films should depend upon irradiation temperatures and light intensities, having a variety of features in LC droplets or polymer networks such as size, shape, and dispersity.

Polymerization-induced phase separation is generally known as a complex phenomenon controlled by a variety of factors [3]. At a molecular level, it can be presumed that the polymerization should proceed under mutual interactions of growing polymer chains, LC molecules, and the substrate surfaces depending upon polymerization temperatures, at which both polymerization rates and dominant LC alignments are determined. These interactions might give rise to inhomogeneity in microscopic LC/polymer domains. In the case of photopolymerization, moreover, it should be taken into consideration that the light used for the photopolymerization must be absorbed, reflected, refracted and scattered while passing through the substrate/organic layers depending upon the progress of phase separation. In other words, light intensity should vary with a great deal of complexity along the vectorial direction of the light beam from the incident substrate surface and also at each point with the progress of phase separation. This means that complex inhomogeneity may occur in microscopic domains of each LC droplet or polymer network along the light beam direction. In the photopolymerized thin film sandwiched between two electrodes, moreover, both LC molecules and polymer chains interact with the electrode surface to form interface layers in which alignments and mobility of LC molecules would be unique and different from those in the interior domain. All these complex features should exert important effects on the electro-optic functions of the LC/polymer composite devices. However, little has been investigated on microscopic domains in LC/polymer films prepared by photopolymerization.

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Analysis of such microscopic domains requires effective methods that are sensitive enough to allow the detection of a limited number of molecules and the estimation of molecular mobility and/or aggregation. Fluorescence techniques have been used as a highly sensitive probe to explore molecular aggregation and microscopic environments surrounding fluorophors, particularly in recent years for microscopic analysis of polymer materials [4]. As our first attempt at the analysis of microscopic domains in LC/photopolymer composite films, the fluorescence behaviour of LC molecules in an interface layer in contact with the substrate surface was investigated by means of 'total-internal-reflection' [5] and 'surface-limited' excitation methods, using the typical nematic LC, 4-cyano-4′-pentylbiphenyl (5CB) [6] and some diacrylates as the materials. It has been found that the fluorescence behaviour of 5CB is considerably different between the interface layer and the interior region depending upon photopolymerization conditions as well as upon the diacrylate structures.

2. Experimental

The 5CB was donated from Lodic Co. Ltd. and used as received. The prepolymers used were three different diacrylates (Nippon Kayaku) abbreviated as **A**, **B**, and **C**, the structures of which are shown in figure 1. Irgacure 184 (Ciba Geigy) was used as the initiator for the photopolymerization. Optically flat quartz plates, indium–tin oxide glass plates (ITO), and semicylindrical sapphire prisms were used as the substrates. Mixtures containing 5CB and one of the diacrylates at various weight ratios and the photoinitiator (1 wt %) were sandwiched between two substrates with 11 μm thickness for fluorescence measurements or 200 μm for scanning electron microscope (SEM) observations and thermal behaviour analysis, and then photopolymerized by irradiation through both of the two substrates or, in particular cases, through one side of the substrates at 25 ± 1 or 50 ± 1°C using a high-pressure mercury arc (Phillips SP-500 W) combined with a neutral glass filter and a cut-off (<310 nm) glass filter. The light intensity at 366 nm was monitored with a UVP UVX digital radiometer and was set to 10 or 40 mW cm^{-2}. The composite films photopolymerized by both-side irradiation are abbreviated as **IIA**, **IIB**, or **IIC** films for each diacrylate **A**, **B**, or **C** used as the prepolymer, and **IA** films denote those obtained by one-side irradiation of 5CB/diacrylate **A** mixtures.

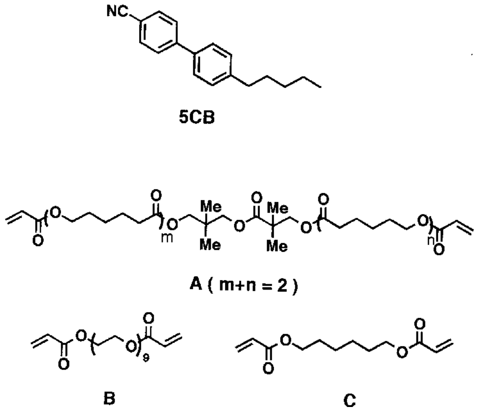

Figure 1. The structures of 5CB and diacrylates **A**, **B**, and **C**.

Distributions of LC domain sizes were analysed by means of a light-scattering method on a Shimadzu SALD-2000. The thermal behaviour of typical **IIA** films was analysed on a Perkin–Elmer DSC7 differential scanning calorimeter. SEM observations of morphological features for typical **IIA**, **IIB**, and **IIC** composite films (76 wt % 5CB) were carried out on a Hitachi S-430 scanning electron microscope after sputtering of Pt with 3 nm thickness on the samples; composite films with 200 μm thickness sandwiched between two glass substrates were washed with hexane to remove 5CB, dried under vacuum, and then broken or separated from the substrates in liquid N_2 to give samples for SEM observations of the sectional or surface views. UV-absorption spectra were taken on a Hitachi U-3500 spectrophotometer for particularly thin films of <100 nm thickness, since the 11 μm thick films containing >1 wt % 5CB showed only the complete light absorption at <320 nm. For the preparation of the particular films, 5CB/diacrylate mixtures were spin-coated on a quartz or ITO plate by using a Mikasa 1H-DXII spin coater, covered with another quartz plate, and then photopolymerized. The film thickness was measured by ellipsometry using a Photo Device MARY-102 automatic ellipsometer for films coated on ITO before photopolymerization.

Fluorescence spectra were obtained on a Hitachi F-4500 spectrofluorimeter, the cell compartment of which was kept at 25 ± 1°C. Composite films sandwiched between two quartz plates were placed diagonally in a quartz cuvette to make an angle of 45° to the excitation light beam, so that the fluorescence light emitted in a direction orthogonal to the excitation light beam was able to be monitored. Slits were attached to both the excitation and emission sides of the quartz cuvette to minimize stray-light effects. In 'surface-limited' excitation experiments, the films were excited at 270–290 nm where the optical densities of the films are extremely large (*vide infra*), so that the excitation light beam can penetrate only a very short depth (⩽100 nm) to excite those 5CB molecules in this limited interface region. In this case, the fluorescence emitted from the front surface was monitored (see figure 2 (*a*)). On the other hand, the excitation light beam at ⩾320 nm can pass through the

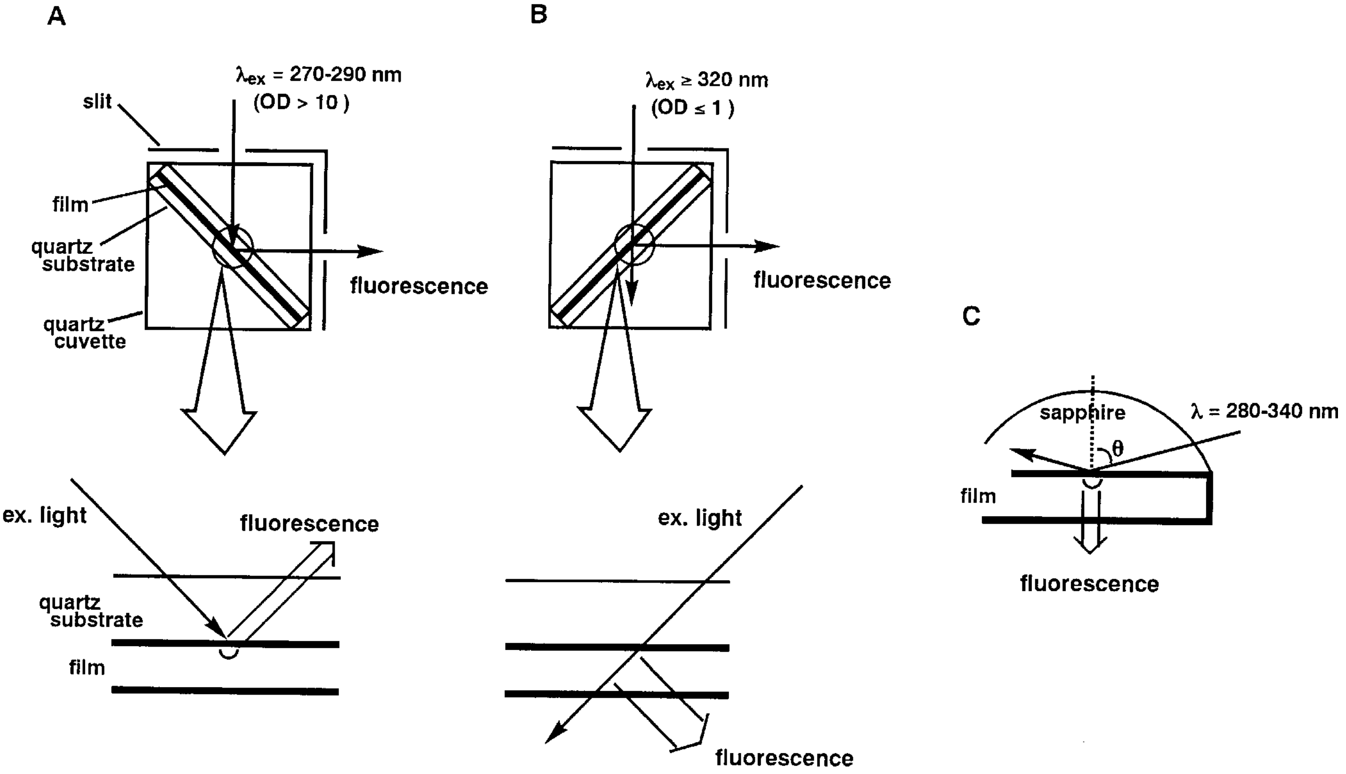

Figure 2. Cell arrangements for fluorescence measurements by (*A*) surface-limited excitation, (*B*) through-film excitation, and (*C*) total-internal-reflection excitation.

film to excite 5CB molecules present along the light path across the film, since the optical densities are less than unity. We call this 'through-film' excitation. The fluorescence taken by this method should be mostly attributable to the emission from the interior domain of the film, since contributions of the interface-layer emission should be negligibly small. In this case, the fluorescence emitted from the rear side was monitored (see figure 2 (*b*)).

As an alternative approach, the interface fluorescence was measured by means of a 'total-internal-reflection' excitation method using sapphire prisms [5]. A composite film was sandwiched between a semicylindrical sapphire prism and a quartz plate, and the excitation light was introduced into the sapphire prism through an optical fibre/lens system to make various incident angles at the flat surface (see figure 2 (*c*)). In cases where the incident angle (θ) is larger than the critical angle, total reflection of the incident light occurs at the interface to bring about the penetration of evanescent light into the film with an extremely short distance. For incident light at $\lambda = 280$–340 nm, the penetration depth (d) of evanescent light was calculated according to equation (1) to be *c.* 150 nm at the critical angle ($\theta \sim 60°$), *c.* 100 nm at $\theta \sim 70°$, or *c.* 50 nm at $\theta \sim 85°$ using the refractive indices of sapphire ($n_s = 1{\cdot}77$) and the film ($n_f \approx 1{\cdot}5$). At $\theta \geq 60°$, therefore, the fluorescence detected is attributable to that from a limited interface region where the evanescent light penetrates, while no fluorescence comes from the deeper interior region. At $\theta < 60°$, on the other hand, no total reflection occurs at the interface, but the incident light can pass through the film at $\lambda > 320$ nm or can cause the surface-limited excitation at $\lambda = 280 \pm 10$ nm.

$$d = (\lambda/2\pi)(n_s^2 \sin^2 \theta - n_f^2)^{-1/2} \qquad (1)$$

3. Results and discussion

The fluorescence behaviour of 4-cyano-4′-alkylbiphenyl (*n*CB) has been well investigated for homogeneous solutions [7] as well as for pure materials [8]. Excited-singlet *n*CB (^1nCB*) strongly emits at ~330 nm with a short lifetime (~1 ns) at low concentrations (equation (2)) and competitively forms the excimer $^1(n\text{CB})_2^*$ at higher concentrations which efficiently emits at ~400 nm with a longer lifetime (~10 ns) (equation (3)) [7]. For convenience, the shorter- and longer-wavelength emissions are hereafter abbreviated as 'monomer emission' and 'excimer emission', respectively. In the nematic phase of neat *n*CB, the excimer emission appears exclusively because of the molecular core packing is favourable for the excimer formation [6, 8], whereas the excimer formation is less efficient in the smectic A phase of higher viscosity [6 (*a*), 8 (*b*)]. In the

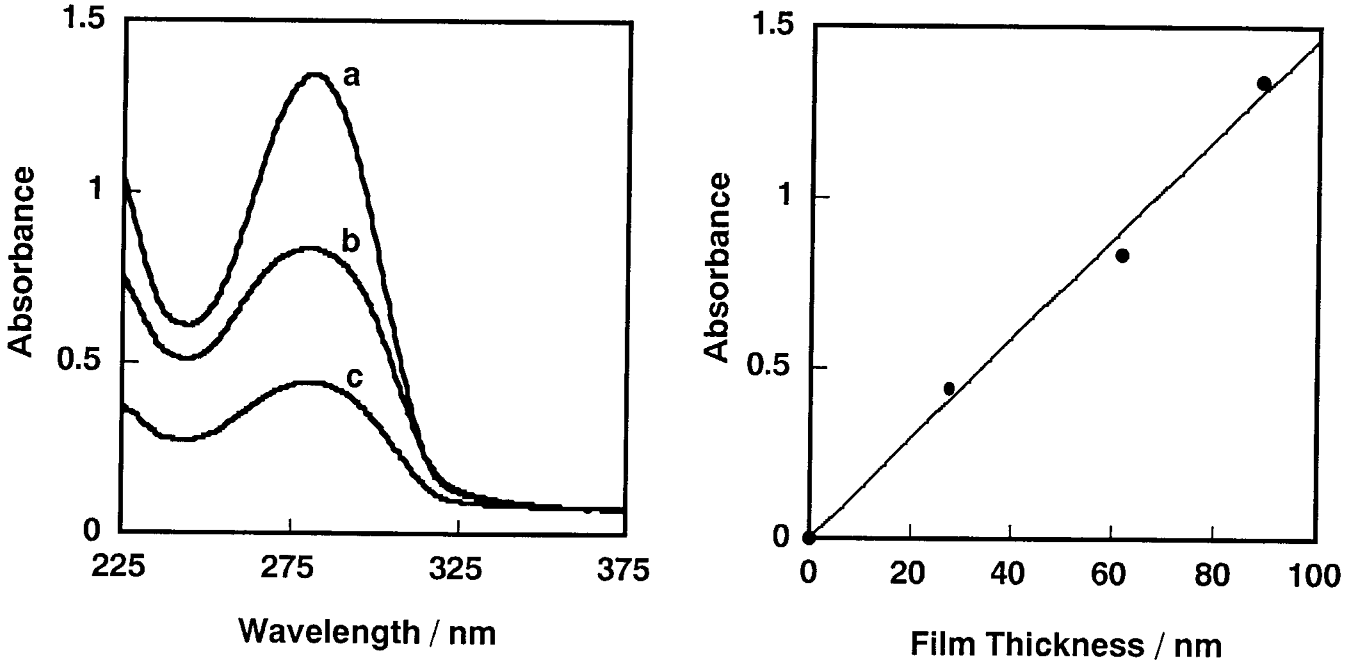

Figure 3. UV-absorption spectra of a **IIA** film (30 wt % 5CB) sandwiched between two quartz plates with (*a*) 88·8 nm, (*b*) 61·4 nm, and (*c*) 27·5 nm thickness (left) and a plot of absorbance at 280 nm versus film thickness (right); the film was prepared at 25°C under UV irradiation at 2·3 mW cm^{-2}.

isotropic phase, on the other hand, both the monomer and excimer emissions comparably contribute to the net fluorescence [6, 8], since randomly oriented *n*CB molecules must reorient and diffuse in the viscous fluid to form the excimer in competition with the fast decay of ^1nCB*. In the present investigation, therefore, relative intensities of the excimer and monomer emissions (I_E/I_M) were used as a convenient probe for the estimation of molecular alignments and mobility of 5CB in composite films.

$$5CB + h\nu \rightarrow {}^1 5CB^* \rightarrow 5CB + h\nu_M \quad (2)$$

$$^1 5CB^* + 5CB \rightarrow {}^1(5CB)_2^* \rightarrow 5CB + 5CB + h\nu_E \quad (3)$$

Figure 3 shows the UV-absorption spectra of particularly thin **IIA** films containing 30 wt % 5CB. The spectra are essentially identical with those of 5CB/diacrylate **A** mixture films before photopolymerization and also very similar to those of 5CB in dilute ethyl acetate solution, thus indicating that the formation of a discrete dimeric species of 5CB absorbing the light at $\lambda > 300$ nm should be negligible. The linear correlation of absorbance with film thickness gives the absorption coefficient, $1{\cdot}46 \times 10^{-2}$ nm^{-1} at 280 nm or $1{\cdot}35 \times 10^{-2}$ nm^{-1} at 290 nm, indicating that the incident light at $\lambda = 280 \pm 10$ nm penetrates into only a limited layer of < 100 nm depth for the films of 30 wt % 5CB and into a still thinner layer for films with higher 5CB content. At $\lambda > 290$ nm, on the other hand, the penetration depth of the incident light increases with the increase of wavelength, and the light at $\lambda \geqslant 315$ nm can pass through films of 11 μm thickness, even for neat 5CB. These observations provide a basis underlying the 'surface-limited' and 'through-film' excitation methods.

Figure 4 shows typical fluorescence spectra of different films. A **IIA** film of 1 wt % 5CB gave only the monomer

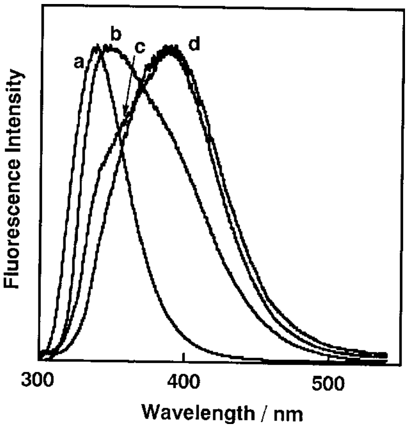

Figure 4. Fluorescence spectra of (*a*) a **IIA** film of 1 wt % 5CB, (*b*) a film of 50 wt % 5CB/diacrylate **A** mixture before polymerization, (*c*) a **IIA** film of 50 wt % 5CB, and (*d*) a neat 5CB film with 11 μm thickness, measured at 25°C by excitation at 290 nm; the composite films were prepared at 25°C by UV irradiation of 5CB/diacrylate **A** mixtures at 40 mW cm^{-2}.

emission at $\lambda = 335$ nm with a single exponential decay of 1·1 ns, in contrast to the exclusive appearance of the excimer emission from a neat 5CB film; no LC domain should be involved in the **IIA** film. While a mixture of 50 wt % 5CB and diacrylate **A** before photopolymerization showed the monomer emission accompanied by a minor contribution of the excimer emission, the dominant appearance of the excimer emission occurred for the **IIA** film prepared by photopolymerization of the mixture. A time-resolved analysis of the emission from the **IIA** film of 50 wt % 5CB was performed at $\lambda = 360$ nm, giving a major decay component of 11·1 ns and a minor one of $<0{\cdot}5$ ns, in accord with the excimer formation associated with quenching of ^{1}5CB*. These observations clearly demonstrate the formation of LC domains by photopolymerization-induced phase separation. Since phase-separated LC domains form the nematic phase (*vide infra*) at 25°C where fluorescence measurements were performed, the excimer $^{1}(5\mathrm{CB})_2{}^{*}$ must be exclusively formed, as described above. Before photopolymerization, on the other hand, the inefficient excimer formation should arise from a diffusional encounter of randomly distributed 5CB molecules in the very viscous homogeneous mixture in competition with the rapid decay of ^{1}5CB*.

Figure 5 shows DSC thermograms of a typical **IIA** film (76 wt % 5CB) and neat 5CB. The **IIA** film stripped from quartz substrates gave a broad endothermic thermogram possessing two maxima at 29·5 and 30·3°C, which is attributed to the nematic–isotropic phase transition of the 5CB domains. This clearly indicates that the composite film contains phase-separated LC domains which should be dominant in the nematic phase at 25°C, where the fluorescence measurements were carried out. However, it is of interest to note that the **IIA** film gave the broader two endothermic peaks at slightly lower temperatures with a lower ΔH value compared with the single sharp peak of neat 5CB. Presumably, the nematic 5CB domains in the composite film might be in less uniform and/or less ordered molecular aggregation compared with that of neat 5CB, arising from interactions of 5CB molecules with the polymer surface.

The fluorescence spectra of a **IIA** film (38 wt % 5CB) in figure 6 were taken by excitation at 275, 300, and 320 nm, clearly indicating greater contributions of the excimer emission (i.e. $I_{\mathrm{E}}/I_{\mathrm{M}}$) at the longer excitation wavelengths. As already mentioned, the surface-limited excitation at 275 nm gives the emission from a very thin interface layer (<100 nm), whereas the emission obtained by the through-film excitation at 320 nm mostly arises from the interior bulk. The excitation light at 300 nm must be scavenged within a very short distance but can reach a deeper region than the 275 nm light can, thus giving net fluorescence involving comparable contributions from both the interface layer and a part of the interior bulk. It is therefore suggested that 5CB molecules in the interface layer should be in unique environments different from those in the interior bulk. Since the $I_{\mathrm{E}}/I_{\mathrm{M}}$ value of the interface emission is smaller than that of the interior emission, molecular alignments and/or mobility of 5CB in this layer should be less favourable for the excimer formation than those in the interior bulk, perhaps arising from interactions of 5CB molecules with the substrate surface and/or from smaller sizes of LC domains in the interface layer compared with those in the interior bulk.

Since the light passing through such inhomogeneous materials as the present composite films must be

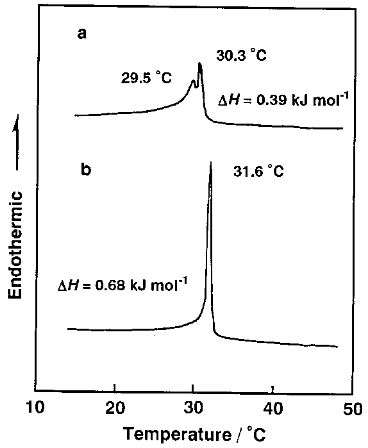

Figure 5. DSC thermograms of (*a*) a **IIA** film (76 wt % 5CB) and (*b*) neat 5CB; the **IIA** film with 200 μm thickness was prepared at 25°C under UV irradiation at 2·3 mW cm^{-2}. The heating scan was performed from 10 to 60°C at a rate of 5°C min^{-1}.

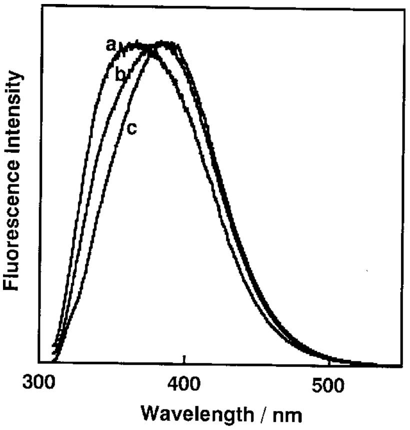

Figure 6. Fluorescence spectra of a **IIA** film (38 wt % 5CB) by excitation at (*a*) 275 nm, (*b*) 300 nm, and (*c*) 320 nm, measured at 25°C with the cell arrangements *A* and *B* in figure 2, respectively; the film was prepared at 25°C under UV irradiation at 10 mW cm^{-2}.

scattered, the fluorescence spectra would be more or less susceptible to such light-scattering effects. It should be noted however that the fluorescence spectrum taken by the surface-limited excitation is almost identical with those obtained by the total-reflection excitation with the cell arrangement C in figure 2, even though the emitted light directly comes from the ultrathin interface layer in the former case but through the composite film in the latter (*vide infra*). Moreover, it was confirmed that the fluorescence spectra of a composite film taken with the cell arrangements A and B in figure 2 show very similar dependence on the excitation wavelength, though different degrees of light-scattering effects would occur with these cell arrangements. According to these results, light-scattering effects should be negligible or may not be important in the present discussions on the fluorescence spectra.

Alternatively, the dependence of the fluorescence spectra on the excitation wavelength would be attributable, at least in part, to the formation of a 5CB dimer in the ground state [6], if the dimer would absorb the light at >300 nm to give the excimer emission. However, the absorption spectra of film **IIA** in figure 3 reveal no indication for the possible formation of such a discrete dimeric species having light absorption at >300 nm. As shown in figure 7, moreover, the fluorescence spectra taken by the total-internal-reflection method are virtually independent of the excitation wavelengths and very similar to that obtained by the surface-limited excitation (see figure 6). Therefore, such a dimer may not be taken into consideration for the wavelength dependence of the fluorescence spectra in figure 6, though the formation of dimeric species having no absorption at >300 nm cannot be excluded [6]. It is of practical significance to note that the surface-limited excitation method can be conveniently used for measurements of the interface-layer fluorescence as effectively as the total-reflection method.

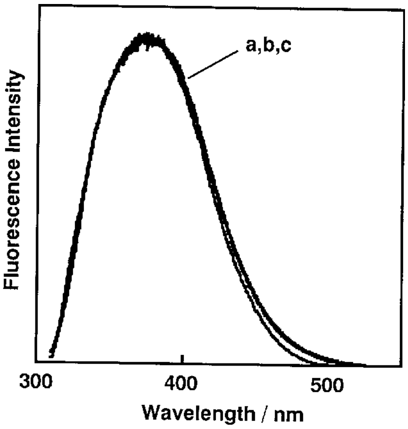

Figure 7. Fluorescence spectra of a **IIA** film (38 wt % 5CB) by total-reflection excitation at (*a*) 275 nm, (*b*) 300 nm, and (*c*) 320 nm, measured at 25°C with the cell arrangement *C* in figure 2; the film was prepared at 25°C under UV irradiation at 10 mW cm^{-2}.

Table 1 summarizes the dependence of I_E/I_M on 5CB concentration as well as on photopolymerization temperatures for the interface-layer and interior-bulk emissions of various **IIA** films; the interface-layer and interior-bulk emissions were obtained by the total-reflection and through-film excitation at 320 nm respectively. The I_E/I_M values are the ratios of corrected emission intensities at 335 and 400 nm, which were calculated by subtracting contributions of the excimer or monomer emission from the net emission intensities at each wavelength. For the calculations, the spectra of the **IIA** film (1 wt % 5CB) and the neat nematic 5CB film in figure 4 were used as references for the monomer and excimer fluorescence spectra, respectively. The greater I_E/I_M values at higher 5CB contents can be easily understood, since greater degrees of phase separation should occur upon photopolymerization at higher contents of 5CB to give a larger number of LC droplets with greater sizes and, at the extreme, a continuous LC phase in a polymer network.

The dependence of I_E/I_M on the polymerization temperatures suggest that temperature-dependent phase separation should occur to result in different molecular alignments and/or different droplet sizes in either the interface layer or the interior bulk. As shown in figure 8, the **IIA** films of 76 wt % 5CB prepared at 25°C and 50°C have different distributions of LC droplet sizes, which give mean sizes of 2·408 ± 0·232 μm and 1·280 ± 0·304 μm, respectively. Although the light-scattering method may not be a reliable means to determine absolute domain sizes for such LC/polymer composite films, it was confirmed that the above values are well correlated with the domain sizes estimated from SEM observations. Therefore, the observed values can be safely used, at least, for relative evaluation of the domain sizes. At the lower temperature, mutual solubility of 5CB and growing polymers should be lower to cause

Table 1. Intensity ratios of excimer and monomer emissions (I_E/I_M) for the interface layer and interior bulk of **IIA** films prepared at 25°C and at 50°C.

		I_E/I_M (interface)[†]		I_E/I_M (interior)[‡]	
polymerization temperature/ °C	5CB wt%	38	76	38	76
25		1·73	2·51	1·92	3·51
50		1·16	2·37	1·83	3·19

[†] Measured by the total-internal-reflection method using the 320 nm excitation light at the incident angle of 85°.

[‡] Measured by the through-film excitation at 320 nm.

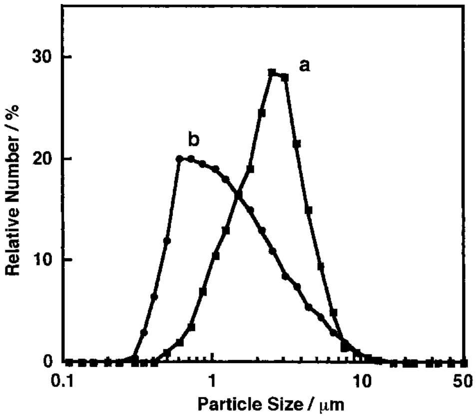

Figure 8. Particle size distributions in **IIA** films (76 wt % 5CB) prepared (*a*) at 25°C and (*b*) at 50°C under UV irradiation at 10 mW cm^{-2}.

an earlier progress of the phase separation associated with the formation of larger LC droplets. An interesting speculation is that 5CB molecules might be more impregnated in the polymer matrix at the higher temperature to contribute, at least in part, to the lower I_E/I_M value. Moreover, it should be taken into consideration that the LC domains formed by phase separation are nematic at 25°C but isotropic at 50°C. At the different temperatures, therefore, different environments at interfaces with the polymer and substrate materials might be formed under different mutual interactions of the relevant materials in the progress of phase separation.

In the case of a **IA** film (38 wt % 5CB) fabricated by irradiation through one of the two substrates, significantly different fluorescence spectra were obtained upon exciting each of the interface layers at 290 nm, as shown in figure 9. For convenience, the interface layer in contact with the substrate through which UV light for photopolymerization was *not introduced* is abbreviated as the 'unirradiated' interface layer and the other as 'irradiated'. The spectrum of the unirradiated interface layer is very similar to that of the interior bulk enriched by the excimer emission, but significantly different from that of the irradiated interface. Therefore, the unirradiated interface layer appears to form a continuum with the interior domain unlike the irradiated interface layer. This means that the formation of the 'unique' interface layer in contact with the irradiated substrate surface might proceed not only under interactions of relevant organic molecules with the substrate surface but should be also controlled by complex factors, for example, inhomogeneity in photopolymerization arising from such optical effects as reflection, refraction, and scattering of UV light in the progress of phase separation as well as from local heating in the vicinity of the irradiated substrate surface.

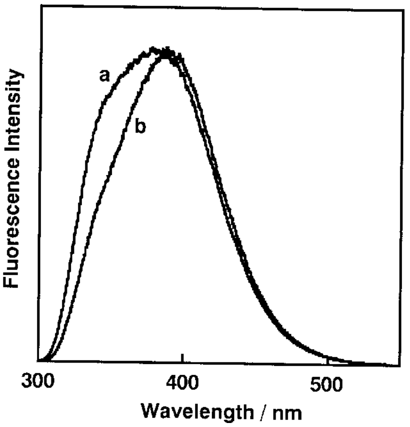

Figure 9. Fluorescence spectra of a **IA** film (38 wt % 5CB) by excitation at 290 nm (*a*) through the substrate irradiated for photopolymerization and (*b*) through the unirradiated substrate, measured at 25°C; the film was prepared at 25°C under UV irradiation at 40 mW cm^{-2}.

The fluorescence behaviour was also found to be substantially affected by the diacrylates used, as shown in table 2 for **IIA**, **IIB**, and **IIC** films of 38 wt % 5CB. The excimer emission is considerably more dominant for the **IIB** film compared with the other films, and the I_E/I_M values of the **IIB** and **IIC** films are less dependent upon the excitation wavelengths than those of the **IIA** film. It is of interest related with the fluorescence results to note that SEM observations of **IIA–C** films (76 wt % 5CB) showed different morphological features (see figure 10). In the cases of **IIA** and **IIC** films, sample films for SEM analysis of the surface image were easily obtained by peeling off the glass substrates. On the other hand, the **IIB** film gave only the sectional view, since it was not possible to peel off the substrates. At any rate, the SEM observations clearly indicate larger sizes of LC domains in the **IIB** film compared with those of the **IIA** and **IIC** films, being apparently in accord with the differences in I_E/I_M since the excimer formation seems to be more favourable in larger LC domains. The differences in I_E/I_M as well as in morphological features might originate from the different structures of the diacrylates. Diacrylate **C** has the more rigid, much shorter, and less polar hexamethylene chain than the

Table 2. Intensity ratios of excimer and monomer emissions (I_E/I_M) for **IIA**, **IIB**, and **IIC** films (38 wt% 5CB) prepared at 25°C.

	I_E/I_M		
λ_{ex}/nm	**IIA**	**IIB**	**IIC**
290	1·68	4·03	1·55
300	2·25	4·33	1·67
310	2·34	4·42	1·78

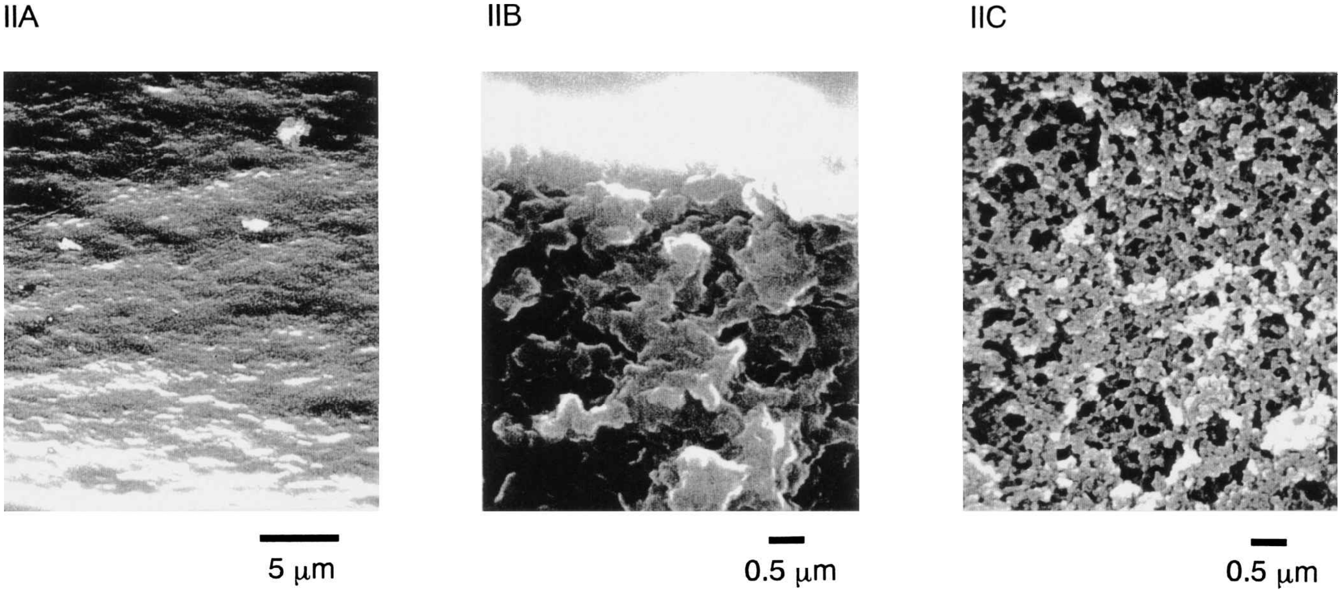

Figure 10. Scanning electron microscope observations of **IIA** and **IIC** polymer films (surface view) and of a **IIB** polymer film (sectional view) obtained by removing 5CB from the corresponding **IIA–C** films (76 wt % 5CB) with 200 μm thickness; film preparation was carried out at 25°C by UV irradiation of 5CB/diacrylate mixtures at 10 mW cm^{-2}.

other diacrylates, and the linkage of diacrylate **A** is longer and bulkier than that of diacrylate **B**. The structure differences should cause different interactions of growing polymer chains with 5CB molecules as well as with the substrate surface to exert significant effects on the progress of phase separation associated with different features of LC domains in either the interface layer or the interior bulk.

4. Conclusions

The present investigation has demonstrated that the fluorescence methods using the excimer and monomer emissions of 5CB as the probe are potentially useful and sensitive for characterizing molecular alignments and/or mobility of 5CB in the interface layer in contact with the substrate surface and in the interior bulk of composite films prepared by photopolymerization of 5CB/diacrylate mixtures. It has been shown that the 5CB excimer is less prevalent in the interface layer than in the interior domain. This was attributed to molecular interactions with the substrate surface that should form a particular interface layer different from the interior bulk to 'freeze' the mobility and alignment of the 5CB molecules unfavourably for excimer formation. Moreover, intensity ratios of the excimer and monomer emissions for either the interface layer or the interior domain have been found to show a substantial dependence on the photopolymerization conditions as well as on the diacrylate structures, being related with different features of photopolymerization-induced phase separation.

It is of practical significance to note that the surface-limited excitation method using 5CB as the *intrinsic* fluorescence probe is much more convenient than, and as effective as a more sophisticated one, the total-internal-reflection method, for fluorescence analysis of the interface layer. It can therefore be expected that this method is widely applicable to analysis of interface layers in other LC/polymer composite devices. Another effective way for the analysis of interface layers is the use of an *extrinsic* fluorescence probe covalently bonded with a solid surface to detect changes of relevant microscopic environments [9]. A key to this approach is the choice of desirable fluorescence probes, such that the fluorescence chromophore must be free from interactions with the solid surface but may show high responses to environmental changes in an interface layer. Work in this line is now in progress.

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